

# Interactions of Aniline with Soil and Groundwater at an Industrial Spill Site

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The interactions of aniline with soil at an industrial spill site were investigated. Sorption of aniline to the soil was observed to occur through a two-step mechanism. The first step was an ion exchange process with the protonated amine serving as an organic cation. This step was influenced by solution pH and ionic composition. The second step was covalent bonding most likely with quinone moieties and oxidation with polymerization of aniline. The extent of covalent bonding was influenced by the presence of oxygen and redox potential. The majority of aniline that was bound to the soil did not readily desorb under a variety of abiotic conditions. However, aniline was released to a significant extent in the presence of denitrifying and methanogenic microbial activity. Aniline in aqueous solution was readily biodegradable under aerobic and denitrifying conditions. Soil-bound aniline was observed not to be biodegradable. This paper provides an overview of results. — *Environ Health Perspect* 103(Suppl 5):71–73 (1995)

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## Introduction and Overview of Results

Aniline-contaminated soil investigated in this study was obtained from an anonymous chemical manufacturer. Approximately five hectares of land area were contaminated to an unknown depth. Aniline was used as a raw material for a variety of chemical processes. The contamination had occurred by two methods. First, aniline was spilled onto the ground during the manufacturing process spanning several decades. Second, at least 40,000 pounds of aniline were spilled at the site in 1979.

Two primary objectives were the focus of this research project. The first, more fundamental and theoretical objective was to describe the mechanisms of interaction between aniline and soil. The second objective, an extension of the first, was to develop an effective remediation process for aniline-contaminated soil. Although some experiments were designed to evaluate specific remediation processes, all experimental results provided information on the fundamental interactions between aniline and soil.

Development of a remediation process for a contaminated soil system should be based on a thorough understanding of the contaminant–soil interactions. The forces of attraction between contaminants and soil and the partitioning of a contaminant among soil solution, soil gas phase, contaminant condensed phase, and soil mineral and organic fractions are all thermodynamic phenomena. Rates of adsorption, desorption, surface reactions, biotransformation, and biodegradation are quantifiable with chemical reaction models. Mass transport and process rate limitations must be understood and minimized for extractive or bioremediation process development. Thus, both chemical and microbial interactions occurring within the soil–contaminant system were the focus of this study.

Sorption of a variety of organic contaminants onto soil has been investigated due to their direct effects on groundwater contamination. The forces of attraction that have been most commonly attributed to interactions of organic contaminants within soil systems include solubilities in water, hydrophobic interactions, induced dipoles with negatively charged functional groups, and solvation forces with soil organic matter (1,2). Although these forces are undoubtedly important for aniline–soil interactions, the results from this project indicate that ionic and covalent bonding are the predominant forces controlling aniline sorption in soil. This sorption process appears to occur in two phases. The first phase is very rapid and is comprised primarily of ionic bonding with cation exchange sites. The second phase is the gradual devel-

opment of one or more types of covalent bonds with the soil organic matter.

The effect of solution pH provided the most dramatic evidence for the ionic bonding phase of the sorption process. Depending on solution pH, the rate of aniline sorption could be predicted with ionization equilibrium constants for aniline and humic acid. Slightly acid pH conditions resulted in maximum attraction between aniline and soil due to the positive charge acquired by aniline and the negative charge on soil mineral and organic fractions. At a solution pH near 3.0, the permanent negative charge on soil was counteracted by protonation of various organic functional groups. Consequently, at low pH, the soil developed a neutral or even positive net charge resulting in reduced attractive forces with aniline and a reduced rate of sorption. Under alkaline conditions, both the pH-dependent and permanent cation exchange capacity combined for a large negative charge. However, aniline is essentially neutral at high pH, which also resulted in reduced attractive forces and, consequently, reduced rate and extent of aniline sorption.

Analogous to the effect of pH on the soil cation exchange capacity, the negative charge exhibited by a soil at a given pH is also a function of the type and content of clay minerals and organic matter. The rate and extent of aniline sorption onto the uncontaminated soil used in this project were significantly lessened by organic matter removal from the soil by thermal oxidation. Essentially no aniline sorbed onto a soil composed of kaolinitic clay with only a trace amount of cation exchange capacity.

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Substantial sorption occurred onto a bentonitic clay soil due to its high cation exchange capacity. Sorption onto pure organic materials was also observed using humic and fulvic acid extracted from an organic soil, as well as just the humic acid fraction after fulvic acid removal. These organic materials exhibited a tremendous sorptive capacity for aniline. The fulvic acid fraction significantly increased this capacity, presumably due to the greater concentration of carboxylic acid groups on this fraction.

The ionic bonding phase of the aniline sorption process was also controlled by mineral cations in solution that compete for negatively charged sites. Calcium was a stronger competitor than sodium due to its divalent charge. Effects on aniline rate and extent of sorption were directly proportional to mineral cation concentrations.

Collectively, these results provide strong evidence for an ionic interaction between aniline and soil. If ionic bonding were the only mode of interaction, then soil-bound aniline would be readily exchangeable by mineral cations. However, experiments conducted on a soil contaminated with aniline resulted in extremely low aniline removals with deionized water, sodium and calcium solutions, or a variety of organic solvents. Quantification of soil-bound aniline concentration was best determined by treatment of contaminated soil with strong caustic solutions combined with an organic cosolvent. Rate of release at ambient temperature was exceedingly slow, requiring several weeks to reach apparent equilibrium. The effect of temperature was significant on the release process. The amount of aniline released with 1N NaOH/50% ethanol at 140°C in 24 hr was twice that released at ambient temperature in 24 days.

Four reaction sequences were proposed to account for the covalent bonding between aniline and soil organic matter. Reactions between aniline and phenol, benzoic acid, benzaldehyde, and benzoquinone were conducted to represent reactions between aniline and functional groups on soil humic matter. Gibbs free energy calculations indicated that reactions with phenol and benzoquinone would be favorable in dilute aqueous solutions. Similar studies reported in the literature suggested that the aldehyde and quinone groups were the primary binding sites for substituted anilines. Results from model reactions in this study discounted the significance of aldehydes and subsequent imine bonds for the covalent bonding of aniline.

Quinones are probably the predominant bonding sites for aniline on soil organic matter. Benzoquinone was the only compound tested to react uncatalyzed with aniline. This reaction was prevented under reducing conditions. Under these conditions, benzoquinone was hypothesized to be reduced to hydroquinone, which was less reactive with aniline. The effect of reducing conditions on lessening the sorption of aniline on soil was presumably due to a similar mechanism. Additional potential reaction sites with aniline other than those investigated in this study may be important due to the complexity of soil organic matter.

Oxygen was observed to have a significant enhancement effect on the formation of covalent bonds, particularly nonhydrolyzable bonds. Oxygen may facilitate oxidation reactions resulting in aniline condensation and polymerization products. The subsequent surface reactions that occur after aniline is bound, which results in attachment to multiple sites, also may be enhanced by oxygen.

Another mechanism by which aniline can become associated with soil organic matter is by oxidation to various condensation and polymerization products. These reactions can be catalyzed by a variety of soil enzymes, oxygen, or oxidizing agents present within the system. Collectively, these compounds have reduced solubility in water, increased attraction toward humic matter, and, consequently, decreased leachability.

Phenolic and carboxylic groups probably have limited involvement in the covalent bonding of aniline to soil organic matter. These reactions have been observed to be catalyzed by soil enzymes (3) and soil microorganisms (4). The potential for amide bonds between aniline and soil humic matter is also supported by the diversity of soil bacteria that can degrade aniline-containing pesticides by breaking amide linkages, which releases substituted anilines (5,6). If aniline is bound by amide linkages, then it is reasonable to suspect that indigenous microorganisms can hydrolyze these bonds, releasing aniline; this represents the mechanism by which soil-bound aniline can be released into groundwater as observed in this study. These studies, however, do not preclude the potential for microorganisms to break other aniline-bonding mechanisms.

Microbial treatment of aniline-contaminated soil with denitrifying and methanogenic anaerobes resulted in

significant amounts of aniline in the liquid phase. Results from desorption and extraction experiments indicated that the aniline was nonextractable. Therefore, the contaminated groundwater at the field site was apparently due, in part, to biologically mediated release. Anaerobic, reduced, and biologically inhibited conditions released only 5% of the quantity released by the active methanogens. It is critically important to determine that the microbially mediated anaerobic release mechanism for aniline is not merely due to hydrolysis.

Aerobic degradation of soil-bound aniline was not observed under the conditions used in this study. A variety of environmental factors that may affect aerobic activities such as moisture content, oxygen content, pH, and cosubstrates, were not evaluated. Thus, the potential still exists for developing an aerobic culture capable of degrading soil-bound aniline. Investigators have observed that aerobic degradation of soil-bound substituted anilines was very slow, indicating that development of this process may be difficult (7-12).

A correlative study of aniline-contaminated groundwater revealed an interesting relationship between aniline concentration and groundwater flow rate. Aniline concentration was positively correlated with groundwater flow rate during high flow rate regimes. These results suggested that dissolution of condensed aniline from micropores was not the only source of groundwater contamination. It was hypothesized that, during high flow conditions, the soil was more saturated and anaerobic and thus may have initiated a release mechanism mediated by anaerobes.

Based on the results of these and other studies reported in the literature, Figure 1 describes the hypothetical distribution of aniline in various states following a spill. The thickness of the arrows reflects the approximate proportions distributed among the respective states. Capillary pressure, London dispersion forces, and ion exchange are among the forces that maintain aniline on soil colloids. Degree of protonation is determined by solution pH. Aniline held by noncovalent forces may be leached to the groundwater or may form covalent bonds with itself by various condensation and oxidation reactions or with the soil organic matter. The latter reactions may result in nonhydrolyzable bonds. Only the aerobic biodegradation of free aniline has been widely observed (13). Covalently bound aniline is aerobically or

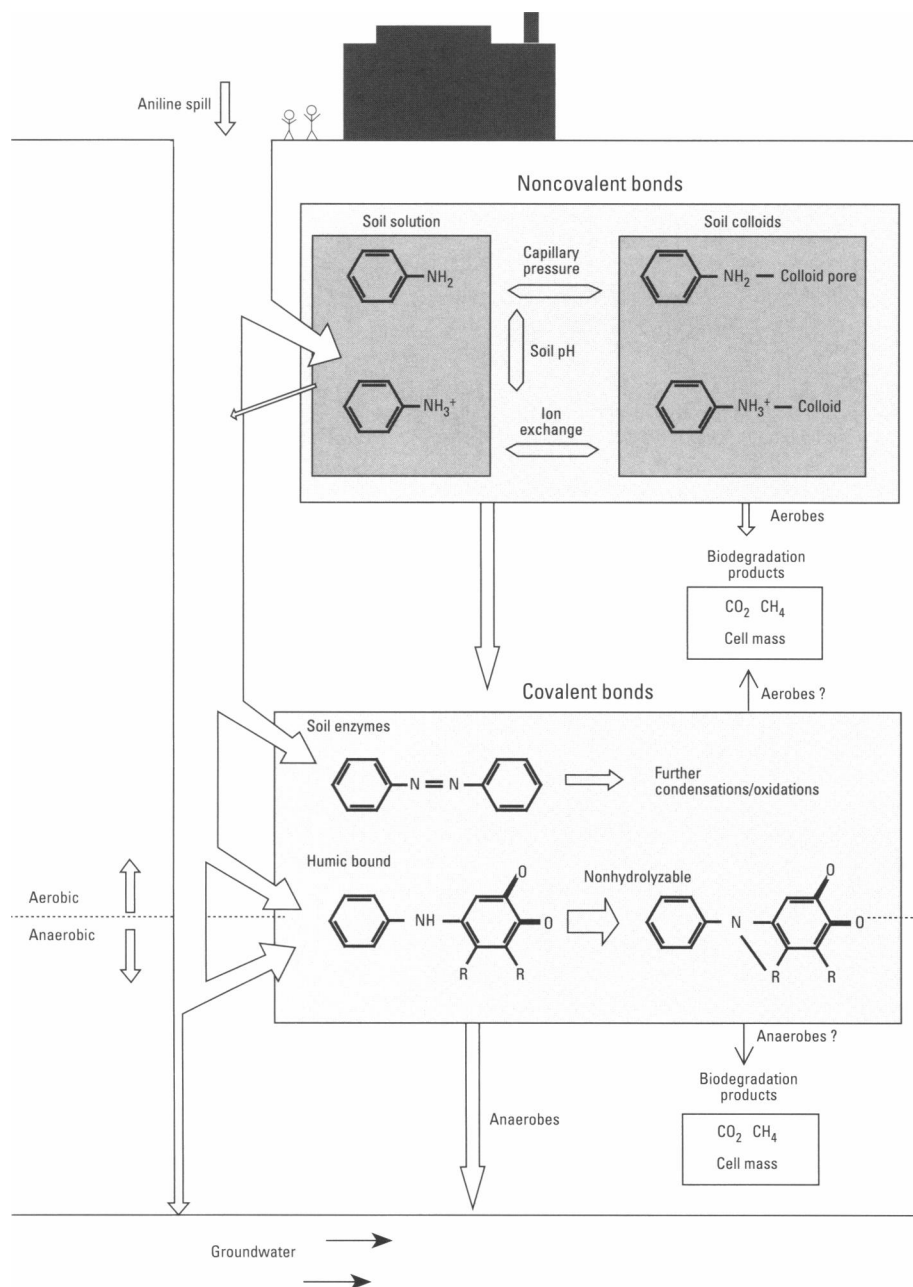


Figure 1. Hypothetical distribution of soil-bound aniline following a spill.

anaerobically biodegraded at very slow rates, if at all. This study indicates that anaerobes may remove aniline from one or more of the covalently bound states. The proportional distributions are likely to change, depending on soil organic matter content, soil texture, soil pH, concentration and quantity of the aniline spilled, and time. For example, a large spill would ini-

tially result in a large proportion reaching the groundwater by channeling through macropores.

The most promising remediation process in terms of effectiveness and cost advantages is the employment of indigenous anaerobes capable of releasing soil-bound aniline. The release rate that has been occurring naturally can potentially be

accelerated. Apparently, indigenous methanogenic activity was limited by the acid pH of the soil. When the acid was neutralized to pH 7.0, significant amounts of methane and free aniline were produced. Indigenous denitrifiers released nearly half of the hydrolyzable aniline in 8 weeks when the soil was provided with nitrate, inorganic nutrients, and acetate.

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